PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : H01J 49/40, 49/16, G01N 15/14 — A1

(11) International Publication Number: **WO 96/31900**

(43) International Publication Date: 10 October 1996 (10.10.96)

(21) International Application Number: PCT/NL96/00141

(22) International Filing Date: 2 April 1996 (02.04.96)

(30) Priority Data:
1000011 3 April 1995 (03.04.95) NL

(71) Applicants *(for all designated States except US)*: STICHTING SCHEIKUNDIG ONDERZOEK IN NEDERLAND [NL/NL]; Laan van Nieuw Oost Indie 131, NL-2593 BM The Hague (NL). STICHTING VOOR DE TECHNISCHE WETENSCHAPPEN [NL/NL]; Van Vollenhovenlaan 659/663, NL-3527 JP Utrecht (NL).

(72) Inventors; and

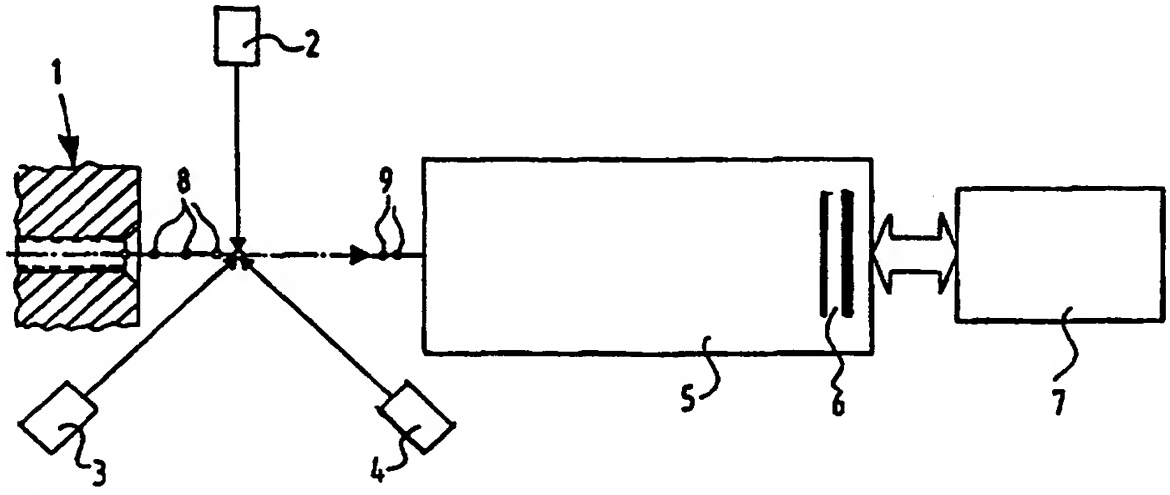
(75) Inventors/Applicants *(for US only)*: KIEVIT, Olaf [NL/NL]; Arthur van Schendelplein 61, NL-2624 CR Delft (NL). WEISS, Martin [NL/NL]; Zusterlaan 184b, NL-2611 MP Delft (NL). MARIJNISSEN, Johannes, Cornelis, Maria [NL/NL]; Zaart 11, NL-4819 ED Breda (NL).

(74) Agent: KUPECZ, Arpád; Octrooibureau Los en Stigter B.V., Weteringschans 96, NL-1017 XS Amsterdam (NL).

(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: A METHOD AND DEVICE FOR THE ANALYSIS OF THE CHEMICAL COMPOSITION OF PARTICLES



(57) Abstract

The present invention relates to a method for the analysis of the chemical composition of particles, which comprises forming a particle-containing flow, detecting the presence of the individual particles, the subsequent fragmentation and ionization of the particles and the identification of each fragment by means of mass spectroscopy, and relates to a device for the analysis of the chemical composition of particles which comprises: bundling means for forming a particle-containing flow; detecting means for detecting the individual particles; fragmentation means and ionization means for the fragmentation and ionization of particles; and a mass spectrometer for the identification of each fragment, wherein the detection means, the fragmentation means and the ionization means each comprise at least a laser generator, wherein the method is characterized by the detection and fragmentation of particles without spacial separation and by the ionization of fragments, and the device is characterized by the fact that the laser beams of the detection means, the fragmentation means and the ionization means are focused onto the same focusing point.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	**GB**	United Kingdom	**MW**	Malawi
AT	Austria	**GE**	Georgia	**MX**	Mexico
AU	Australia	**GN**	Guinea	**NE**	Niger
BB	Barbados	**GR**	Greece	**NL**	Netherlands
BE	Belgium	**HU**	Hungary	**NO**	Norway
BF	Burkina Faso	**IE**	Ireland	**NZ**	New Zealand
BG	Bulgaria	**IT**	Italy	**PL**	Poland
BJ	Benin	**JP**	Japan	**PT**	Portugal
BR	Brazil	**KE**	Kenya	**RO**	Romania
BY	Belarus	**KG**	Kyrgystan	**RU**	Russian Federation
CA	Canada	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CF	Central African Republic			**SE**	Sweden
CG	Congo	**KR**	Republic of Korea	**SG**	Singapore
CH	Switzerland	**KZ**	Kazakhstan	**SI**	Slovenia
CI	Côte d'Ivoire	**LI**	Liechtenstein	**SK**	Slovakia
CM	Cameroon	**LK**	Sri Lanka	**SN**	Senegal
CN	China	**LR**	Liberia	**SZ**	Swaziland
CS	Czechoslovakia	**LT**	Lithuania	**TD**	Chad
CZ	Czech Republic	**LU**	Luxembourg	**TG**	Togo
DE	Germany	**LV**	Latvia	**TJ**	Tajikistan
DK	Denmark	**MC**	Monaco	**TT**	Trinidad and Tobago
EE	Estonia	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**UG**	Uganda
FI	Finland	**ML**	Mali	**US**	United States of America
FR	France	**MN**	Mongolia	**UZ**	Uzbekistan
GA	Gabon	**MR**	Mauritania	**VN**	Viet Nam

A method and device for the analysis of the chemical composition of particles

The present invention relates to a method for the analysis of the chemical composition of particles, which comprises forming a particles-containing flow, detecting the presence of the individual particles, the subsequent fragmentation and ionization of particles and the identification of each fragment by means of mass spectroscopy, and relates to a device for the analysis of the chemical composition of particles which comprises: bundling means for forming a particles-containing flow, detecting means for detecting the presence of the individual particles; fragmentation means and ionization means for the fragmentation and ionization of particles; and a mass spectrometer for the identitification of each fragment, while the detecting means, the fragmentation means and the ionization means each comprise at least a laser generator.

Such a method and device are used for the analysis of ambient air, for instance in a clean-room where products such as chips, are manufactured, which during the production process are particularly sensitive to dust particles floating around in the production room. Further, by means of such a device a quality control for products such as aerosol cans may be carried out. Such a method and device may also be applied for the detection of agents used in chemical or biological warfare or of atmospheric pollution.

Such a method and device is known from the article by Prather, Nordmeyer and Salt (1994), in Anal. Chem. 66: 1403-1407, entitled "Real-time characterization of individual aerosol particles using time-of-flight mass spectrometry".

In this method the time interval between two successive detection signals is used to study the fragmentation and ionization of particles. To this end such a device comprises an electronic timing circuit which measures the delay between two detection signals and activates the fragmentation means and the ionization means on the subsequent arrival of a detected particle in a fragmentation and ionization area, which arrival is established by means of the

measured time interval between the successive detection signals. Such a method, and consequently the appertaining device, is very sensitive to alignment faults. Moreover, the laser fragmentation and ionization means may miss a particle if a beam followed by the particle travels such that said beam does not run exactly parallel to the axis of the formed particle-containing beam.

It is the aim of the invention to eliminate the above-mentioned objections and to this end it provides a method which is characterized by the detection and fragmentation of particles without spacial separation and ionization of fragments, and provides a device which is characterized in that the laser beams of the detection means, the fragmentation means and the ionization means focus onto the same point.

The invention will be further elucidated with reference to the following figure description of an embodiment of the invention. In the drawing

Fig. 1 shows schematically the principle of the method and the device according to the present invention;

Fig. 2 shows a schematically perspective view of the configuration of an embodiment of a device according to the present invention;

Fig. 3 shows a cross-sectional view of a component of the device according to the present invention as shown in Fig. 2; and

Figs. 4 and 5 show embodiments of a nozzle which forms part of the bundling means shown in Figs. 1 and 2.

In the Figures one and the same reference number refers to one and the same part.

The device shown in Fig. 1 comprises: bundling means formed by a particle flow generator 1; detection means formed by a detection laser 2 and detectors; fragmentation means formed by a fragmentation laser 3; ionization means formed by an ionization laser 4; a mass spectrometer 5; and an arithmetic unit 7.

The particle flow generator 1 creates a flow of particles 8, which flow is propulsed under very low pressure, which is necessary to ensure the functioning of the mass

spectromet r 5. The particles are formed by clusters of atoms and molecules, while the gas is removed from the bundled flow of particles 8 in the particle flow generator 1. The spectrometer used is a time-of-flight mass spectrometer necessitating the pressure of the bundled flow particles 8 to be lower than 10^{-4} Pa in order to ensure correct functioning of the spectrometer 5.

The particles 8, formed by clusters of molecules and atoms, are detected in the area of action 13 due to the particles 8 scattering light coming from the detection laser 2, whereby detectors 10 are placed such that they only emit a detection signal if light coming from the detection laser 2 is scattered by a particle 8. Therefore the detection laser 2 need not be of high power so that the detection laser 2 may for instance be a 16 mW multimode HeNe laser.

The fragmentation laser 3 fragmentates the particles into separate atoms and molecules after which the separate molecules and atoms are ionized with the aid of the ionization laser 4. The ions 9 formed in this manner are subsequently analyzed with the aid of the mass spectrometer 5, whereby the data gathered by the mass spectrometer 5, and pertaining to the identity of the ions, are processed by the arithmetic unit 7.

The arithmetic unit 7 also functions as control circuit for the fragmentation laser 3 and the ionization laser 4. In reaction to a detection signal coming from the detectors 10, the arithmetic unit 7 activates the fragmentation laser 3 and the ionization laser 4, so that the arithmetic unit 7 contains data relating to the moment in time at which the ions 9 are created.

In the mass spectrometer 5 an electric field is installed so that a previously known amount of kinetic energy is supplied to the ions 9. The thus accelerated ions 9 then travel over a precisely known distance to an ion-sensitive plate 6 in the mass spectrometer 5, where arrival of the ions is registered by the plate 6. As the moment in time at which the ions 9 are formed and the moment in time at which the ions arrive at the plate 6 are known, the ions and thus the atoms and molecules can be identified from the linear rela-

tion between the mass of the ions 9 and the velocity with which these ions 9 travel the distance between the place of their formation and the plate 6.

The amplitude of the signal generated by the mass spectrometer 5 is a measure of the number of ions arriving at any one moment at the ion-sensitive plate 6. In this way it is not only possible to establish the presence of a type of molecule or atom in a particle 8, but also the amounts of the different atoms or molecules the particle 8 contained for fragmentation and ionization.

Further, the size of a particle 8 that is to be analyzed is determined from the detection signals coming from the detectors 10; this will be described in more detail below.

Fig. 2 shows the configuration of an embodiment of a device according to the present invention comprising: a particle flow generator 1 forming the bundling means; a detection laser 2 appertaining to the detection means; a combination laser forming the fragmentation means and the ionization means; detector appertaining to the detection means forming the photomultiplier tubes 10; a light absorption element 11 and electrode grids 12.

The bundled flow of particles 8 created by the particle flow generator 1 reaches the area of action 13 in which both the detection laser 2 and the combination laser 34 are focused, the particles 8 being propulsed by the particle flow generator 1 at a velocity of about between 200 and 300 m/s. This velocity is realized because the particles are sucked into the vacuum and due to the particle flow generator 1, which will be described in more detail below.

The detection laser 2 sends a laser beam into the direction indicated by the arrow A. The laser beam coming from the detection laser 2 is influenced by the lens 21, the dichroitic mirror 23 and lens 24 such that the resulting focus corresponds with the size of the area of action 13. The size of the area of action 13 and thus the focus is 0,1 mm. The mirror 23 is of such a kind that it only reflects light having the same frequency as that generated by the detection laser 2.

A particle 8 in the ar a of action 13 scatters light coming from the detection laser 2 into all directions, which scattered light is detected with the aid of photomultiplier tubes 10 in the directions indicated by arrows B. The photomultiplier 10 tubes are arranged at an angle of 90° and 45° in relation to the direction of the light coming from the detection laser 2 and falling onto the area of action 13. It is well known in the field of technology that an optimal amount of information relating to scattering can be obtained when detection takes place in the above-mentioned directions.

The light absorption element 11 is arranged in the extension of the direction indicated by arrow A, so that light coming from the detection laser 2 in the direction indicated by arrow C, which is not scattered by a particle 8, is absorbed. This prevents that light wrongly reflected into the direction is deemed scattered light, causing a detection signal to be emitted by the photomultiplier tubes 10 as if a particle 8 were detected in the area of action 13.

This embodiment of a device according to the present invention uses two photomultiplier tubes 10. Detection signals coming from the photomultiplier tubes 10 are only then sent to the combination laser 34 as initiation signal for fragmentation and ionization of the particles 8 present in the area of action 13, if both photomultiplier tubes 10 simultaneously emit such a detection signal. This avoids the combination laser 34 coming into action when there are no particles 8 present in the area of action 13, because this logical "AND" function compensates the adverse inherent property of photomultiplier tubes 10, which photomultiplier tubes 10 emit a detection pulse, even without incident light.

In the configuration shown in this figure, photomultiplier tubes 10 are chosen as detectors, although also a number of other detectors such as photodiodes, are known in the filed of technology. This was decided because photomultiplier tubes have a very short reaction time (approx. 2 ns), a very high amplification factor (approx. between 10^3 and 10^8), and a very large active surface (up to maximally 97 cm^2), and at the same time a superior signal-noise ratio.

The photomultiplier tubes 10 are preferably protected against high power laser pulses coming from the combination laser 34 by means of filters (not shown).

In order to compensate differences in amplitude among the detection signals emitted by the photomultiplier tubes 10, a lens 26 is placed in front of the photomultiplier tube 10 detecting scattered light under an angle of 90°. In another embodiment of the invention (not shown) a lens can also be placed in front of the photomultiplier tube 10 detecting scattered light under an angle of 45°, in order to increase the intensity of the scattered light detected by the photomultiplier tube 10, and thereby increasing the sensitivity of the configuration.

In reaction to detection signals from the photomultiplier tubes 10 subjected to a logical "AND" function, the combination laser 34 is activated, whereby this combination laser 34 is a pulsating Nd:YAG laser having an intensity of approx. $3 \cdot 10^{14}$ W/m², which suffices both to fragmentate particles 8 and to ionize fragments of particles 8 to ions 9. Because this Nd:YAG laser generates radiation of more than one frequency, this laser is able to provide fragmentation as well as ionization. In the shown embodiment of the device the flash lamps of the laser 34 pulsate at a fixed frequency of 10 Hz, and a Q-switch is controlled by the detection signals. When detection signals are simultaneously emitted by the photomultiplier tubes and the flash lamps of the laser are charged, the Q-switch is opened to let a short-time pulse of intensive rays through. The laser beam generated by the combination laser 34 is focused through the lens 22 and through the lens 24 to the area of action 13 in the direction indicated by the arrow D, while the mirror 23 forms practically no impediment to the laser beam.

The area of action 13 is formed by the joint focusing point of the laser beams coming from the detection laser 2 and the combination laser 34. The focusing point is formed such that it has a diameter of about 0.1 mm. With the aid of lenses the beam coming from the detection laser 2 can theoretically be focus d to a diameter of 16 μm, but the somewhat larger focusing point provides the laser beam coming from the

detection laser 2 with an optimal chance f accurate aim. In addition, it is easier to align the focused laser beams coming from the detection laser 2 and the combination laser 34 than when the focusing point has a diameter of 16 μm.

A particle 8 detected in the area of action 13 is, as a result of the high power of the combination laser 34, fragmentated and ionized, after which the thus formed ions 9 are sensitive to the electric fields provided with the aid of the electrode grids 12. The ions are accelerated in the direction of the plate 6 of the mass spectrometer 5. As the travel direction of the particles 8 is perpendicular in relation to the travel direction of the ions 9 formed from the particles 8, and as the moment in time at which the ions 9 were formed from the particles 8 is exactly known, reliable operation of the mass spectrometer 5 is ensured.

When, with the aid of the method according to the present invention, the particles 8 are analyzed, the size of the particles 8 is important as well as the chemical composition. The size of the particles 8 can be established bas d on the intensity of the light scattered by a particle 8, which intensity is measured by the photomultiplier tubes 10. There is a direct relation between this intensity of the scattered light and the size of the particle 8 scattering the light. However, this method of determining the size of a particle 8 is not in all cases completely reliable, because a particle 8 travelling partly through the focus of the laser beam coming from the detection laser 2 may scatter light having fractionally the intensity of the light that would be scattered by a particle 8 travelling completely through the focus of the laser beam coming from the detection laser 2. In this configuration in Fig. 2 this problem is solved by placing grid 25 before the detection laser 2, so that the laser beam coming from detection laser 2 creates an interference pattern (shown at the bottom of this Figure) in the area of action 13, whereby the distance between the maxima of the interference pattern is exactly known. By measuring the travelling time of the detected particle 8 between the successive maxima of the interference pattern from the photomultiplier tubes 10, the velocity of the particle 8

travelling through the interference pattern can be determined, whereby the size of this particle 8 is established in relation to the velocity of the particle 8. The element used to create an interference pattern may be a grid 25 or, for instance a beam divider (not shown). Alternatively it is also possible to solve the problem by designing the particle flow generator 1 such that it forms a beam so narrow that all particles travel completely through the area of action 13. However, this solution often imposes limitations on the design of the particle flow generator 1.

If so desired, a separate ionization laser 4 may be provided in the configuration shown in Fig. 2 which could, for instance, be formed by a pulsating UV-laser. This pulsating UV-laser increases ionization of the fragments of particle 8 consisting of molecules and atoms, which particle 8 was fragmentated with the aid of a laser beam formed by the combination laser 34 or with the aid of a laser beam formed by a separate fragmentation laser 3.

Fig. 3 shows a particle flow generator 1, which particle flow generator 1 is attached air-tight to a housing 15. This housing 15 comprises a chamber 14 comprising an area of action 13, whereby the electrode grids 12 are arranged at either side of the area of action 13. The housing 15 is further provided with connecting tubes 16 to which in any case the mass spectrometer 5 is attached air-tight, while to another connecting tube 16 in the drawing at the rear the light absorption element 11 is airtight attached. The laser beams coming from the detection laser 2 and the combination laser 34 are directed (not shown) onto the area of action 13 through a transparent key element attached to a connecting tube 16. Further, each of the photomultiplier tubes 10 is attached air-tight to one of the connecting tubes 16. In this way a chamber 14 is formed, of which the only link with the environment is the particle flow generator 1.

The atmospheric pressure of an environment to be analyzed is usually 10^5 Pa. Reliable application of a time-of-flight mass spectr meter requires that a particle flow is formed having a vacuum-approximating pressure of maximally

10^{-4} Pa. In view of the fact that the available present-day pressure-reducing means, in this case the pumps 17, are able to effectuate per stage a pressure reduction with an approximate factor of 1000, it follows, that three pressure-reducing stages are required in order to obtain a pressure in the chamber 14 of maximally 10^{-4} Pa.

Further, the particle flow should have a very high streamflow-velocity. This shortens the time required for analysis, which is particularly advantageous when measurements are carried out on samples of a low concentrations of particles. However, the streamflow-velocity is directly dependent on the pumps 17 being used; to obtain a high streamflow-velocity large and costly pumps 17 are required, making an analysis device bulky and costly. Consequently, this constitutes a parameter to be considered when designing the device.

The streamflow-velocity is determined by the size of the nozzle's 18 orifice, provided the ratio between the pressure before the nozzle 18 and the pressure after the nozzle 18 is greater than the critical threshold value:

$$\frac{P_b}{P_o} = 0.5283$$

In this case the gas containing the particles reaches the velocity of sound at the exit of the nozzle 18, accelerating, after the nozzle 18, up to supersonic velocity in the travel direction of the gas. If the diameter of the orifice of the nozzle 18 is 0.3 mm, the streamflow-velocity will be approximately 0.9 l/min.

If the gas containing the particles is sucked through a small nozzle orifice into the low-pressure chamber, the gas will rapidly expand with diverging flowlines. Because of their inertia, particles present in the gas do not follow the flowline and the particles continue their linear path. In this way the particles are separated from the gas and a particle-containing beam is formed. The nozzle 18 discharges into a space between the nozzle 18 and a shear element 19, which space is connected with a first pump 17.

The beam containing the particles 8 then passes a first shear element 19 which discharges into another space between this shear element 19 and a second shear element 19,

which space is also connected with a separate pump 17. In this way, as described above, gas is drawn off from the beam containing the particles.

The second shear element 19 discharges into the chamber 14 comprising the area of action 13, which chamber is also connected air-tight with yet another separate pump 17.

With each supersonic expansion shock waves may occur in the particle flow generator 1. These shock waves influence the flow of the gas and prevent optimal operation of the particle flow generator 1. Therefore the particle flow generator is designed such that the formation of shock waves is minimalized. Such shock waves will not develop behind a shear element 19 if the distance between the nozzle 18 and this shear element 19 or the distance between a preceding shear element 19 and the shear element 19 is smaller than the distance at which the shock wave has a maximum diameter. For a nozzle 18 having an orifice of 0.3 mm it has been calculated that with a shear element 19 at a distance of 4 mm there will be no adverse effect of a shock wave. This is of particular importance for the distance between the nozzle 18 and the first shear element 19 because the density of the supersonically flowing gas behind this first shear element 19 will be low, so that the adverse influences caused by a shock wave will be reduced considerably.

The shear element 19 which is arranged first in the travel direction of the particles behind the nozzle 18, has an orifice of 0.4 mm to ensure an efficient particle transport and a reasonable load on the pump appertaining to the space behind this shear element. In order to avoid the shock wave here also, although this shock wave is less important, the next shear element, having an orifice of 3 mm, is placed at a distance of 5 mm in the travel direction of the particles 8 behind the preceding shear element.

Further, the design of the particle flow generator 1 is such that the conveyance efficiency of the particle flow generator is constant for en entir sample, irrespective of the siz of the particles. Further, the step in which a sample is taken, is ind pendent of th particle size.

Experimentation has proven that the nozzl 18 shown in Fig. 4 yields the best conveyance efficiency when particles of at least 2 μm have to be analyzed and the nozzle 18 shown in Fig. 5 is the best choice when particles of up to 2 μm have to be analyzed.

The nozzle 18 shown in Fig. 4 may be made by drawing a glass tube in a capillary element, forming a gradually reducing, converging flow channel. This allows an unlimited diameter choice for the orifice 20 of the nozzle 18.

The nozzle 18 shown in Fig. 5 may be made of metal by using the known methods of manufacture. In this case the orifice 20 is formed with the aid of a spark discharge apparatus, a method which is usually applied to make holes having a diameter of at least 0.1 mm. The use of specially designed spark electrodes make it possible, however, to make orifices having diameters of up to 20 μm.

Similar techniques may be used for the manufacture of the shear elements 19.

To realize a pressure of 10^{-4} Pa in the chamber 14, a nozzle 18 shown in Fig. 4 having an orifice of 0.3 mm or a nozzle 18 shown in Fig. 5 having an orifice of 0.2 mm may be used, taking into consideration the pump capacity of the pumps 17.

In the above description the combination laser 34 used is a pulsating Nd:YAG-laser. However, it is just as well possible to use a laser which may be put into operation at any moment, such as a nitrogen laser or an excination laser. In this way the analysis efficiency is raised by a factor of 2000.

CLAIMS

1. A method for the analysis of the chemical composition of particles, which comprises the bundling of a particles-containing flow, detecting the presence of the individual particles, the subsequent fragmentation and ionization of particles and the identification of each fragment by means of mass spectroscopy, **characterized** by the detection and fragmentation of particles without spacial separation and by the ionization of fragments.

2. A method according to claim 1, **characterized** by the fragmentation of particles into separate molecules.

3. A method according to claim 1 or 2, **characterized** by the determination from detection data of the size of each detected particle.

4. A method according to claim 1, 2 or 3, **characterized** by the detection of particles by means of the detection of light scattered by each of the particles.

5. A method according to claim 4, **characterized** in that the light, before being scattered by a particle, is subjected to interference.

6. A method according to any of the preceding claims, **characterized** in that the detection data serve as starting signal for the initiation of fragmentation and ionization of a particle.

7. A method according to any of the preceding claims, **characterized** in that a particle-containing flow is formed by means of drawing in a particle containing sample, a first reduction of pressure, forming a sample-containing beam and a number of successive reductions of the pressure and narrowing of the beam.

8. A method according to claim 7, **characterized** in that the succession of pressure reductions and narrowing of the beam is repeated twice.

9. A device for the analysis of the chemical composition of particles comprising: bundling means for the formation of a particle-containing flow; detection means for the detection of individual particles; fragmentation means and

ionization means for the fragmentation and ionization of particles; and a mass spectrometer for the determination of the identity of each fragment, wherein the detection means, the fragmentation means and the ionization means each in any case comprise a laser generator, **characterized** in that the laser beams from the detection means, the fragmentation means and the ionization means are focused onto one and the same point.

10. A device according to claim 9, **characterized** in that the detection means comprise at least one detector f r the detection of light scattered by a particle, which light comes form the laser generator appertaining to the detection means.

11. A device according to claim 10, **characterized** in that each of the detectors comprises a photomultiplier tube.

12. A device according to claim 10 or 11, **characterized** in that the detection means comprise more than one detector.

13. A device according to claim 12, **characterized** by a arithmetic circuit to apply the logical "AND" function to the detection signals coming from the detectors.

14. A device according to claim 12 or 13, **characterized** in that at least one of the detectors detect scattered light under an angle of 90° and at least one of the remaining detectors detects scattered light under an angle of 45°.

15. A device according to one of the claims 9 to 14, **characterized** by combination means for the simultaneous fragmentation and ionization of particles, which combination means comprise at least a laser generator.

16. A device according to claim 15, **characterized** in that the combination means are connected with the output of the (or each) detector, while the output signal from the (or each) detector functions as the starting signal for the combination means.

17. A device according to claims 13 and 15, **charact t rized** in that the combination means are connected with the output of the detectors via the arithmetic circuit.

18. A device according to any of the claims 9 to 17, **characterized** in that the mass spectrometer is a time-of-flight mass spectrometer.

19. A device according to claim 18, wherein the time-of-flight mass spectrometer comprises an ion detector detecting, at a previously known distance from the place of ionization, the accelerated ions travelling, after ionization, in an electromagnetic field through a vacuum, **characterized** in that the mass spectrometer comprises an electromagnetic mirror to reflect the ions for their detection.

20. A device according to any of the claims 9 to 19, **characterized** in that the bundling means comprise a nozzle, pressure-reducing means and narrowing means for the narrowing of the beam, wherein the nozzle forming the entry of the bundling means is connected with the space containing the particles to be analyzed and wherein the exit of the bundling means is connected air-tight with the space containing th focusing point.

21. A device according to claim 20, **characterized** in that the narrowing means comprise at least one shear element, wherein the space between a shear element and the nozzle or between a first shear element and a second shear element is connected air-tight with the pressure reducing means.

22. A device according to claim 20 or 21, **characterized** in that the pressure reducing means comprise at least one pump.

23. A time-of-flight mass spectrometer comprising an ion detector registering the arrival, at a known distance from the place of ionization, of ionized ions accelerated by means of an electromagnetic fields in a vacuum, **characterized** by an electromagnetic mirror for reflecting ions for their detection.

24. A particle flow generator for the generation of a flow of particles, **characterized** by a nozzle, pressure reducing means and narrowing means for narrowing the beam.

25. A particle flow generator according to claim 24, **characterized** in that the narrowing means comprise at least one shear element, wherein the space between a shear element and the nozzle or between a first shear element and a second shear element is connected air-tight with the pressure reducing means.

26. A particle flow generator according to claim 24 or 25, characterized in that the pressure reducing means comprise at least one pump.

FIG.1

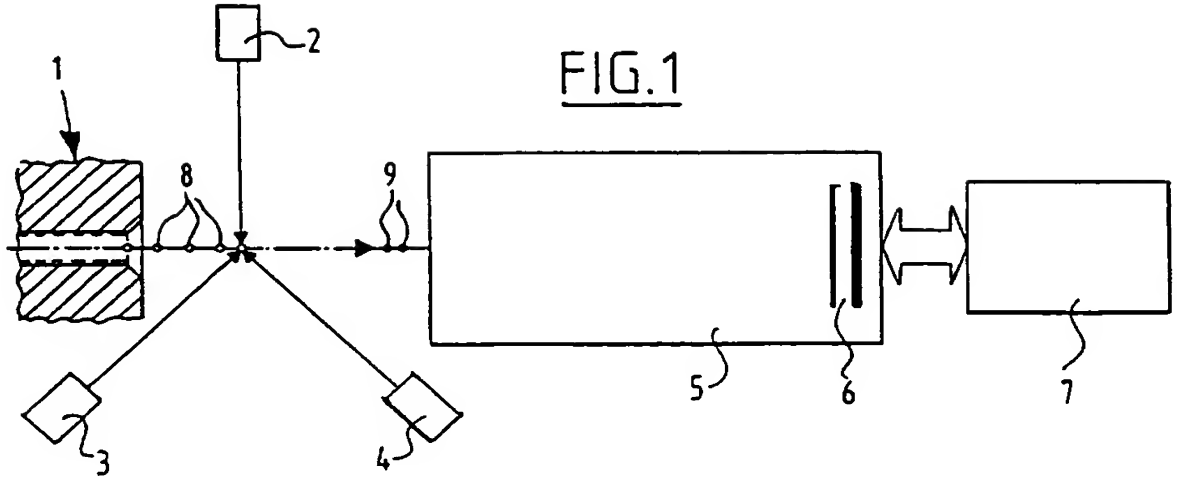


FIG.2

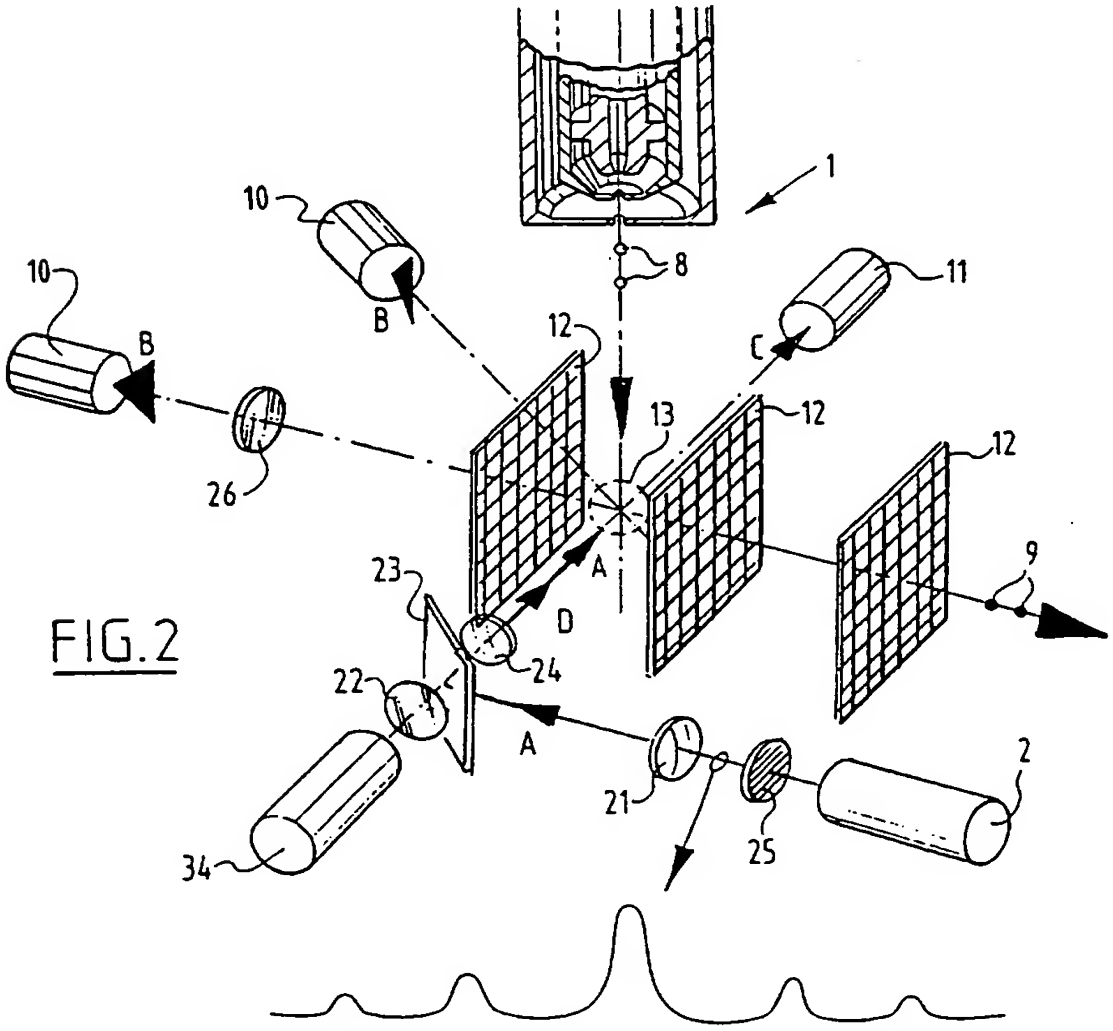
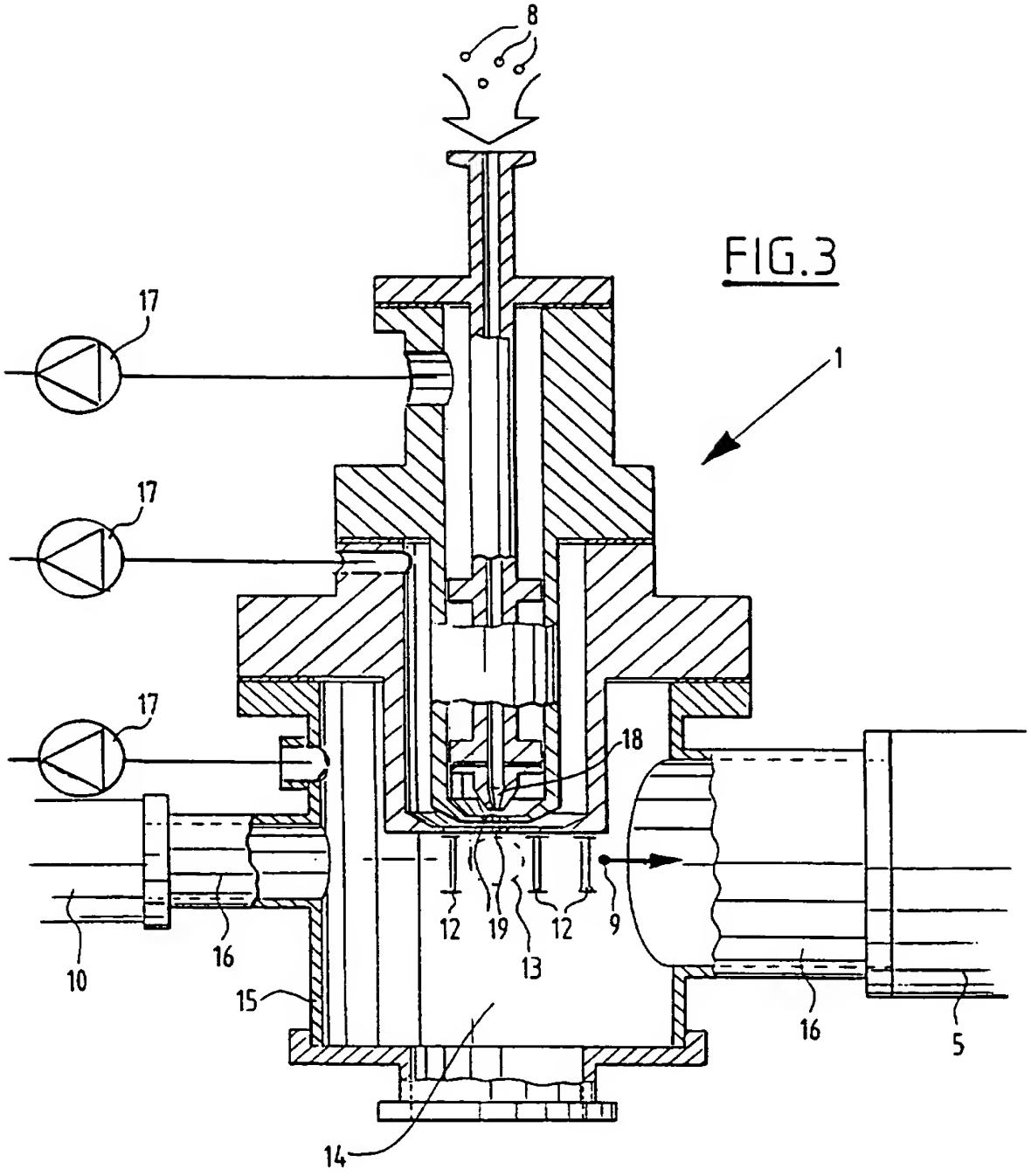


FIG.3



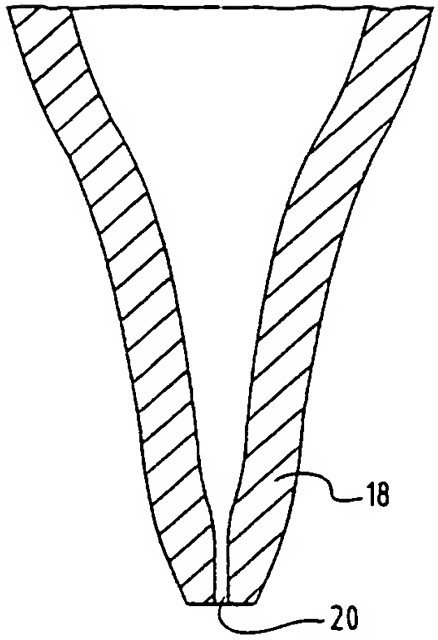


FIG. 4

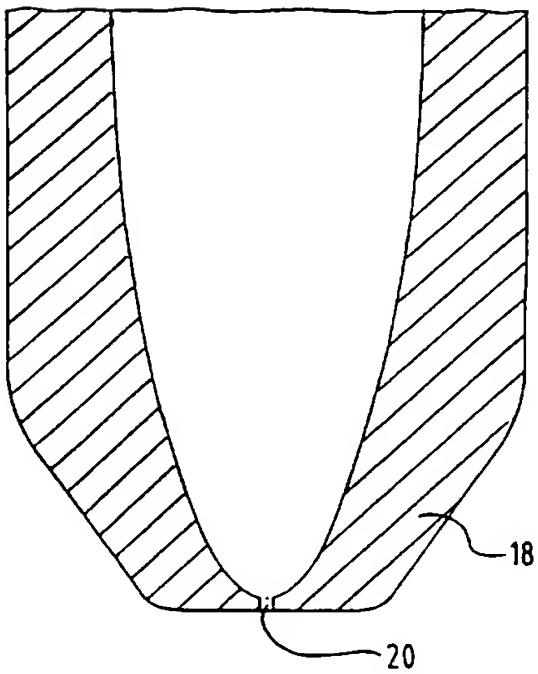


FIG. 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 96/00141

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01J49/40 H01J49/16 G01N15/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ANALYTICAL CHEMISTRY, vol. 66, no. 13, July 1994, COLUMBUS US, pages 2071-2076, XP000455144 HINZ K.-P.: "LASER-INDUCED MASS ANALYSIS OF SINGLE PARTICLES IN THE AIRBORNE STATE" see page 2072, left-hand column, paragraph 3 - page 2074, left-hand column; figures 1,2,6	1-20,22
X	--- -/--	24-26

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 July 1996	12.07.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Hulne, S

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ANALYTICAL CHEMISTRY, vol. 66, no. 9, May 1994, COLUMBUS US, pages 1403-1407, XP000446026 K. A. PRATHER: "REAL-TIME CHARACTERIZATION OF INDIVIDUAL AEROSOL PARTICLES USING TIME-OF-FLIGHT MASS SPECTROMETRY" cited in the application see page 1403, right-hand column, paragraph 3 - page 1404, right-hand column; figure 1	1-4,6,7, 9-13, 15-22
X	see page 1403, right-hand column, line 4 - line 10	23
X	see page 1403, right-hand column, paragraph 3; figure 2	24-26

X	INTERNATIONAL JOURNAL OF MASS SPECTROMETRY AND ION PROCESSES, vol. 131, no. 1-3, 24 February 1994, AMSTERDAM NL, pages 87-124, XP000446266 U. BOESL: "LASER ION SOURCES FOR TIME-OF-FLIGHT MASS SPECTROMETRY" see figure 20	23

A	US,A,4 383 171 (SINHA MAHADEVA P ET AL) 10 May 1983 see column 2, line 14 - column 4, line 34	1,9,24

A	DE,A,40 36 115 (MAX PLANCK GESELLSCHAFT) 14 May 1992	1,9
X	see column 6, line 21 - line 48; figure 4	23

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/NL 96/00141

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4383171	10-05-83	NONE	
DE-A-4036115	14-05-92	US-A- 5365063	15-11-94